

THE INFRARED SPECTRAL ANALYSIS OF CF_2Cl_2

Final Report 712673-1
Grant NAGW-31
February 1984

National Aeronautics and Space Administration
Washington, D.C. 20546

REPORT DOCUMENTATION PAGE		1. REPORT NO.	2.	3. Recipient's Accession No.
4. Title and Subtitle THE INFRARED SPECTRAL ANALYSIS OF CF₂CL₂			5. Report Date February 1984	
7. Author(s)			6.	
9. Performing Organization Name and Address The Ohio State University ElectroScience Laboratory Department of Electrical Engineering Columbus, Ohio 43212			8. Performing Organization Rept. No. ESL 712673-1	
12. Sponsoring Organization Name and Address National Aeronautics and Space Administration Washington D.C., 20546			10. Project/Task/Work Unit No.	
			11. Contract(C) or Grant(G) No. (C) (G) NSGW-31	
			13. Type of Report & Period Covered Final Report	
15. Supplementary Notes			14.	
16. Abstract (Limit: 200 words) The CF ₂ CL ₂ absorption bands at 923 cm ⁻¹ and 1161 cm ⁻¹ are examined as to their detectability in long-path solar spectroscopy. Measurements are reported for a long-path White Cell. A cryo-condensation unit was also constructed to test its ability to improve detection of trace gases in the ambient atmosphere.				
17. Document Analysis a. Descriptors b. Identifiers/Open-Ended Terms c. COSATI Field/Group				
18. Availability Statement		19. Security Class (This Report) Unclassified		21. No. of Pages 27
		20. Security Class (This Page) Unclassified		22. Price

Page intentionally left blank

Page intentionally left blank

TABLE OF CONTENTS

	Page
LIST OF TABLES	iv
LIST OF FIGURES	v
I. INTRODUCTION	1
II. LONG-PATH MEASUREMENTS	7
III. SAMPLE HANDLING	9
IV. AMBIENT SAMPLING	21
REFERENCES	26

LIST OF TABLES

TABLE	Page
I. Rotation and distortion constants to order δ_K for the ground.	13
II. Sample Conditions.	14

LIST OF FIGURES

Figure	Page
1. Low resolution spectrum of CF_2Cl_2 in the region from 800 to 1200 cm^{-1} .	4
2a. Detection of atmospheric CF_2Cl_2 in a ground-based solar spectrum.	5
2b. Detection of atmospheric CF_2Cl_2 in a ground-based solar spectrum.	6
3. Absorption cell and interferometer.	8
4. Geometry of CF_2 molecule. A, B, and C axes are indicated such that $I_A < I_B < I_C$.	11
5a. SAMPLE A.	15
5b. SAMPLE B.	15
5c. SAMPLE C.	16
5d. SAMPLE D.	16
5e. SAMPLE E.	17
5f. SAMPLE F.	17
5g. SAMPLE G.	18
6a. SAMPLE G.	18
6b. SAMPLE B.	19
6c. SAMPLE C.	19
6d. SAMPLE D.	20
6e. SAMPLE F.	20
7. Effects of air broadening on a 0.2 Torr sample of CF_2Cl_2 in a 30 mm cell.	22

I. INTRODUCTION

For many decades the worldwide production of halogen-containing methane compounds has risen rapidly. Two of the most popular compounds are fluorocarbon-11 (CFCl_3) and fluorocarbon-12 (CF_2Cl_2). Their physical properties make these gases ideal for aerosol propellants, refrigerants, and as intermediates in the production of plastics and foams. Once released to the atmosphere, these compounds become uniformly mixed since they are very inert. They slowly diffuse to the upper atmosphere. In 1974, Molina and Rowland [1] suggested that a possible loss mechanism for atmospheric fluorocarbons was photodissociation by ultra-violet radiation in the stratosphere. The dissociation of these molecules produces chlorine atoms which are thought to alter the equilibrium chemistry of ozone in the stratosphere.

The possible destruction of the protective ozone layer was immediately popularized by news media stories even though important quantitative results such as the rates of reaction and concentrations of various fluorocarbons in the stratosphere remained largely unknown. Several groups have performed in situ measurements using gas chromatography [2-4] or infrared spectroscopy [5-7] to detect the presence of CFCl_4 and CF_2Cl_2 in the atmosphere. Infrared spectroscopy from balloon-borne platforms and from ground-based stations which use the sun as a source can achieve very long optical paths through the atmosphere, and therefore are very sensitive methods for observing trace gases in the atmosphere.

There are several NASA programs which are currently scheduled to record infrared spectra from satellite or space shuttle platforms. The one with which the author is most familiar is the ATMOS project being conducted at JPL. In this experiment, infrared spectra from 2 to 15 μm will be recorded at 0.02 cm^{-1} resolution from the space shuttle. The purpose of these high resolution spectra is to obtain a global mapping of trace pollutants. The molecule CF_2Cl_2 will be clearly visible in the collected spectra.

However, before the abundance of a trace gas can be determined from in situ spectroscopic measurements, a thorough laboratory program is needed in order to determine the positions and intensities of absorption lines of the molecule. Furthermore, since the atmosphere is not homogeneous, the variation of spectral features with respect to temperature and pressure must be known. After a complete laboratory study which must include the collection of spectra under a variety of physical conditions (temperature and pressure) has been done, a careful analysis and quantum assignment of the observed absorption lines can be made. From this quantum assignment, a compilation of the line parameters can be made which will include the positions ν , the intensities $S(T)$, and the halfwidths $\alpha(P,T)$ of the individual absorption lines. This absorption line listing can then be used to model the infrared transmittance of the trace gas in the atmosphere.

Compilations of absorption line parameters already exist for many atmospheric cases [8], and programs are in wide use which accurately model the spectral characteristics of atmospheric transmission [9,11].

The purpose of this proposed research program is to analyze several bands of the infrared spectrum of the molecule CF_2Cl_2 . This compound has strong absorption bands near 923 cm^{-1} and 1160 cm^{-1} which have been observed in solar spectra. These results will prove reliable to such in situ projects as ATMOS. Figure 1 shows the absorption spectrum of CF_2Cl_2 throughout the $10\text{ }\mu\text{m}$ region. The sharp Q-branches are ideal spectral features for atmospheric observation of the molecule. Figures 2a and 2b show detection of the sharp Q-branch near 923 cm^{-1} and near 1160 cm^{-1} in ground-based solar spectra.

The spectral region near 923 cm^{-1} is dominated by the ν_6 (B_1) fundamental and is discussed further in the next section. Many overlapping hot bands and isotopic bands complicate this region, however. In a low resolution study, Giorgianni et al [12] found fifteen separate absorption bands which contribute to the total absorption in this region. Thus, a thorough study of this spectral region should eventually include all of these absorption bands.

The existence of hot bands in this region is particularly troublesome for atmospheric modeling since the intensities of different hot bands fall off at different rates depending on the lower quantum state energy level as the temperature is decreased. The importance of these hot bands to the total absorption could be significant, and will be determined by collecting spectra at a variety of temperatures.

The 923 cm^{-1} spectral region is further complicated by the fact that the ν_6 fundamental is known to be in Fermi resonance with a nearby combination band $\nu_3^+ \nu_7$, visible in Figure 1 near 882 cm^{-1} . Thus, even

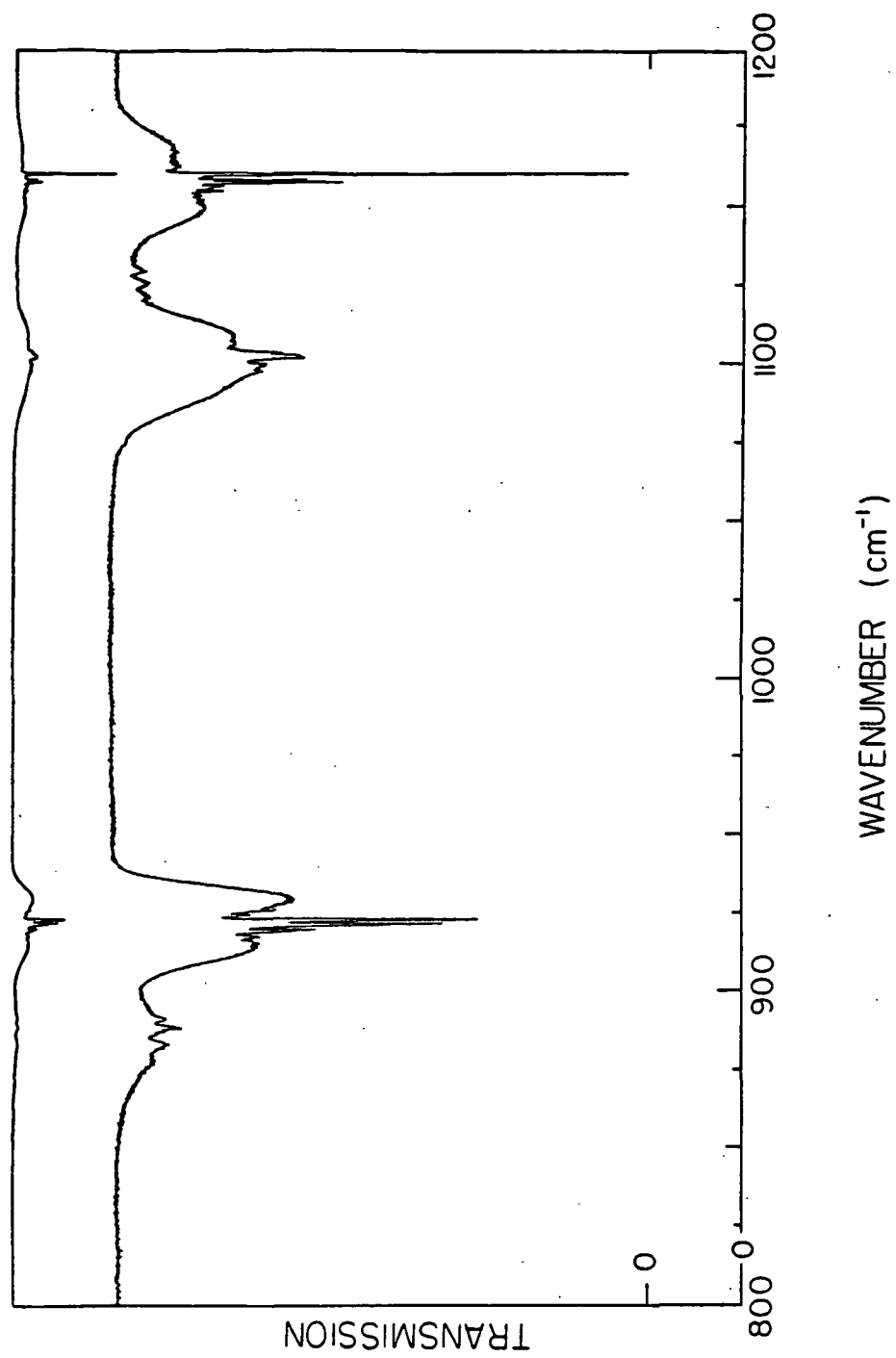


Figure 1. Low resolution spectrum of CF_2Cl_2 in the region from 800 to 1200 cm^{-1} .

OSU SOLAR SPECTRUM

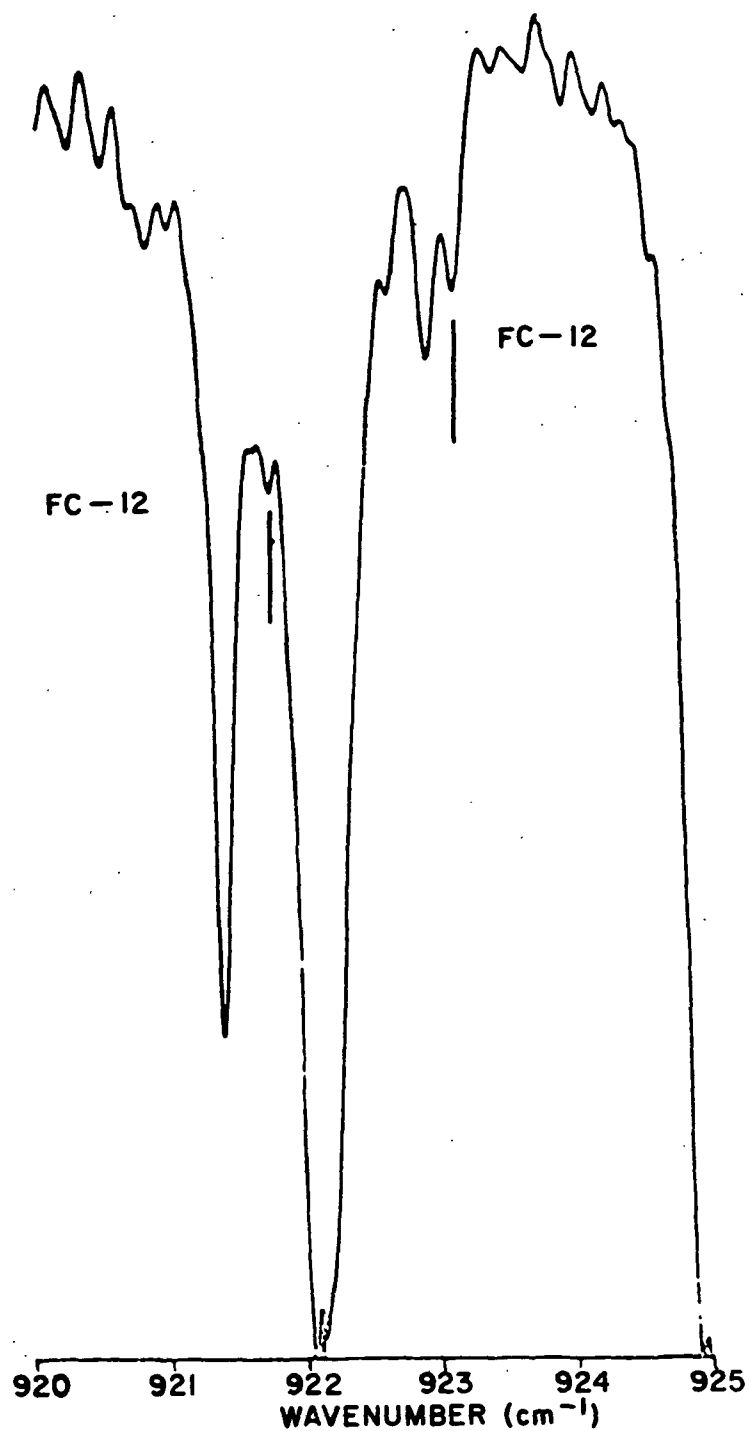


Figure 2a. Detection of atmospheric CF_2Cl_2 in a ground-based solar spectrum.

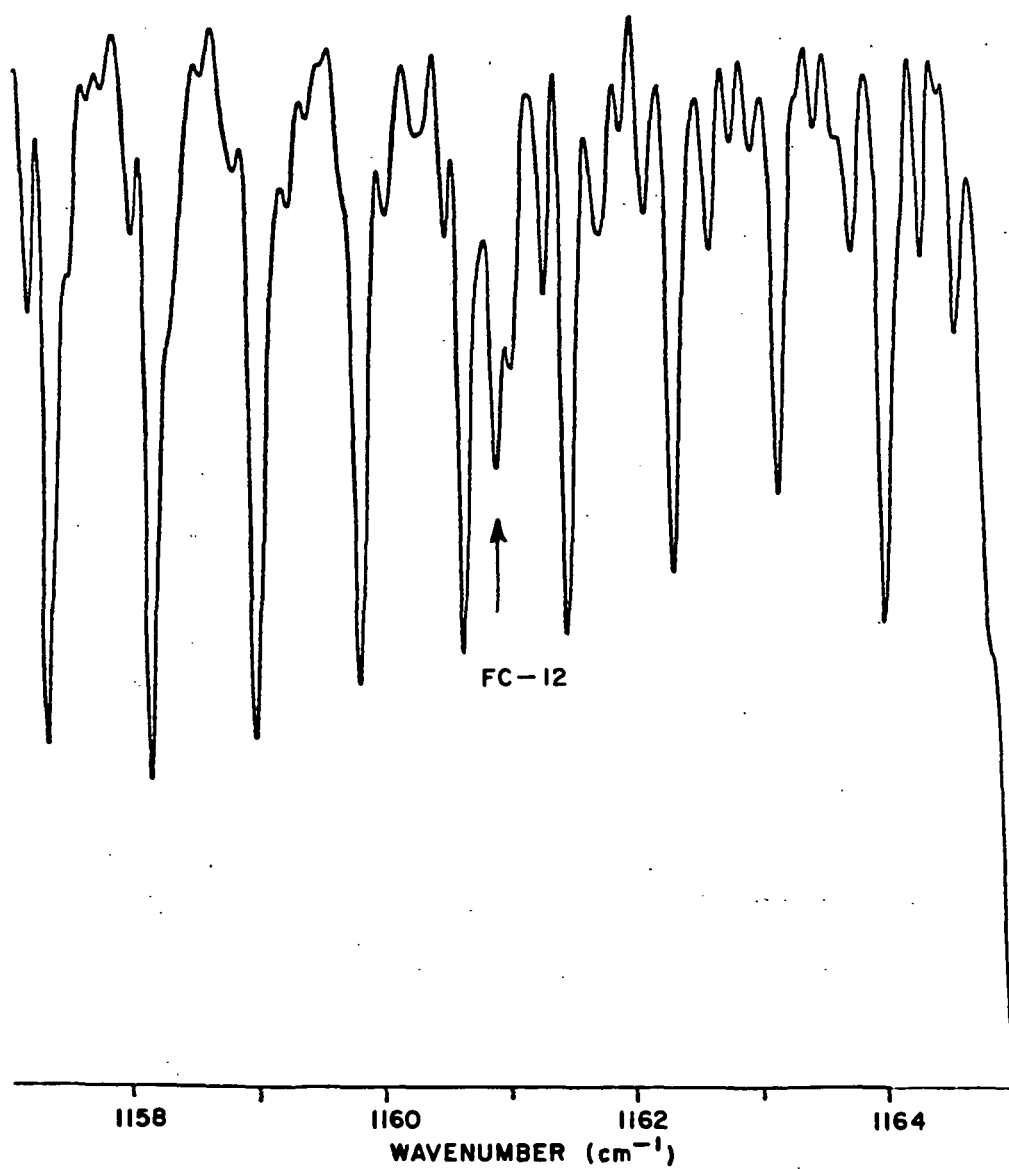


Figure 2b. Detection of atmospheric CF_2Cl_2 in a ground-based solar spectrum.

if several of the interfering bands can be eliminated from analysis because they have negligible effect, many bands still remain which may have to be analyzed simultaneously.

The region near 1160 cm^{-1} is dominated by the ν_8 (B_2) fundamental. Five hot bands also contribute to the total absorption in this region [12]. The ν_8 region has not been looked at in great detail yet although Nordstrom et al [6] found this region more suitable for detection of CF_2Cl_2 in the atmosphere.

II. LONG-PATH MEASUREMENTS

Long-path data were taken in a recently completed White-type cell at the Ohio State University. This cell has been used with its associated Nicolet interferometer at path lengths to one km, and with laser sources to two km paths. A photograph of the cell and interferometer is shown in Figure 3.

The cell body is constructed of type 304 stainless with a 2B interior surface for low vacuum contamination and for work with reactive gases. A vacuum of 3×10^{-6} Torr has been obtained. The cell is 12 meters long and 0.6 meters in diameter. The three mirrors are 25 cm diameter gold-coated Cervit spaced 10.785 m, and with radii of curvature matched to one mm. The optical system is a "double passing" type using a roof mirror, as introduced by Horn and Pimentel. The mirrors are mounted on kinematic mounts of a new design, and attached to the cell mounting base rather than the cell itself for stability over a wide

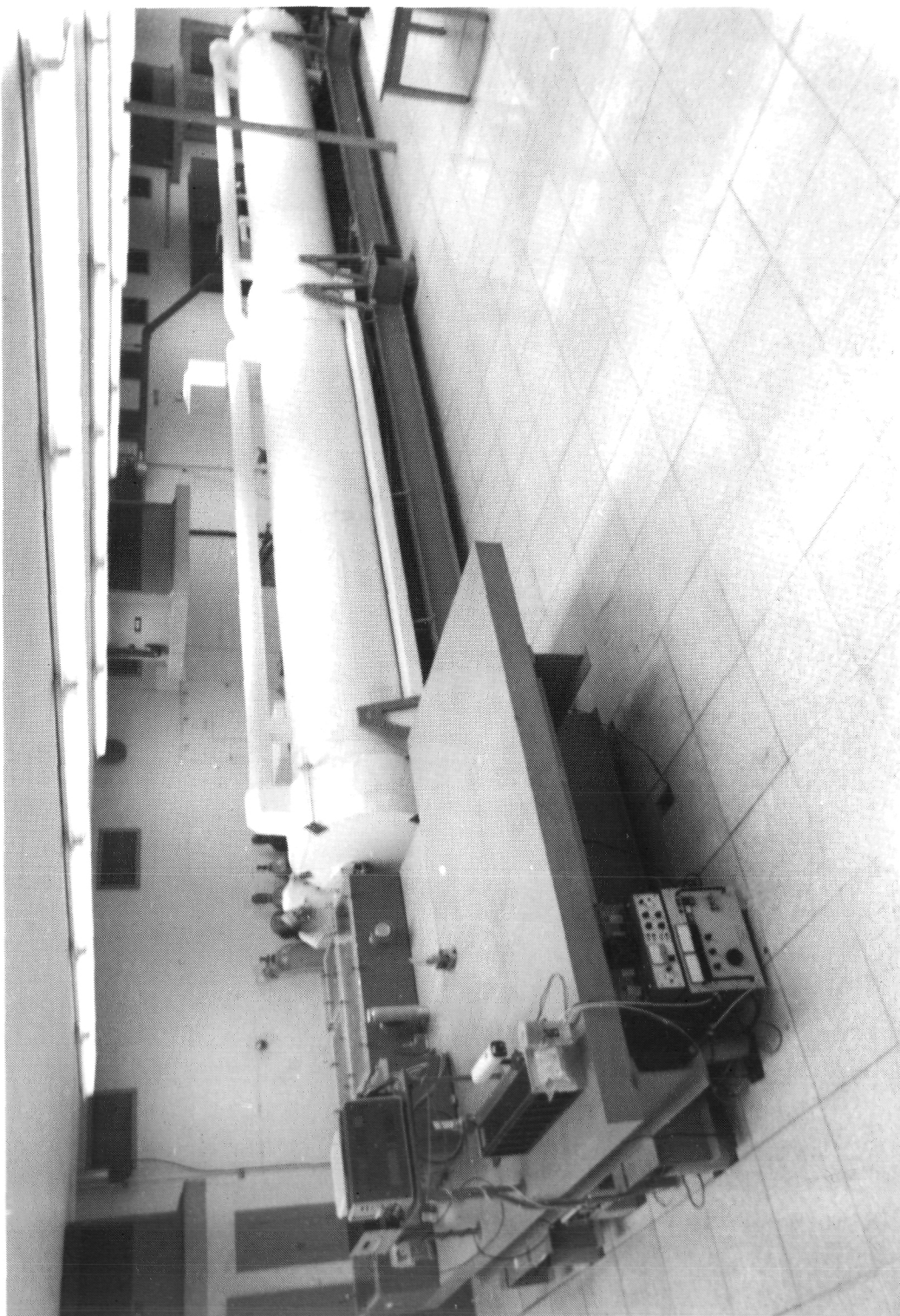


Figure 3. Absorption cell and interferometer.

temperature range. Fine position control of the mirrors is provided by sealed stepper motors controlled by an external computer.

The cell temperature is controlled over the -50C to 50C range by flowing a liquid through tubes welded to the walls. Electrical heat or a cascade mechanical refrigerator is used, and the cell is insulated with 5 inches of fabricated polyurethane.

The cell, optics, and an 8 by 10 foot limestone table are mounted together on a frame made of 12 inch I-beams which in turn is mounted on air supports to limit vibrations.

A Nicolet Model 7199 Fourier transform spectrometer is mounted on the limestone table and optically matched to the absorption system through an evacuable set of transfer optics. A stabilized He-Ne laser controls the Nicolet, and four-hour data sets with resolution of 0.04 cm^{-1} can be routinely obtained. The associated computer collects the data, performs the transform, and plots results.

III. SAMPLE HANDLING

The White cell has several filling ports, either direct (generally used for cell total pressure or dew-point) and one port which goes to the center of a perforated distribution tube extending the length of the cell. This has proved very convenient for assuring well-mixed samples when broadening gases are added. Overnight mixing with circulating fans was previously needed to get homogeneous samples with water vapor; with this tube, samples appear homogeneous within minutes.

For very dilute samples, such as fluorocarbons, an input manifold with three accurately calibrated pyrex sample bulbs is utilized. The manifold, with several gauging and sample ports is connected to three "flow-through" sample bulbs of 5.198 liter, 549 cc, and 62.1 cc volumes. The White cell volume is 3403 liters.

The manifold and sample bulb to be used are evacuated, filled to the desired pressure as determined by a capacitance manometer, and the sample bulb closed off by a Teflon stopcock. The manifold is then re-evacuated, and can be refilled with the broadening gas. The sample is then released into the White cell through a second Teflon stopcock. Although the system was designed to minimize dead volume, it is then flushed with broadener or inert gas to assure that all of the sample reaches the White cell. The bulk of any broadening gas used is generally introduced directly through the distribution tube. Concentrations in the ppm range are thus obtained accurately, and in the ppb range by a single dilution step.

Many spectra of CF_2Cl_2 were recorded under a variety of conditions. A Nicolet Model 7199 Fourier transform spectrometer system was used to collect the data. Maximum resolution of this instrument is 0.04 cm^{-1} unapodized. At this resolution, Q-branch structure of the ν_6 and ν_8 remains unresolved. However, interesting R-branch structure of the ν_6 band and the other overlapping bands is visible.

The CF_2Cl_2 molecule has tetrahedral structure with the carbon atom at the center as shown in Figure 4. This asymmetric-top molecule belongs to the point group C_{2v} when both chlorine atoms are the same

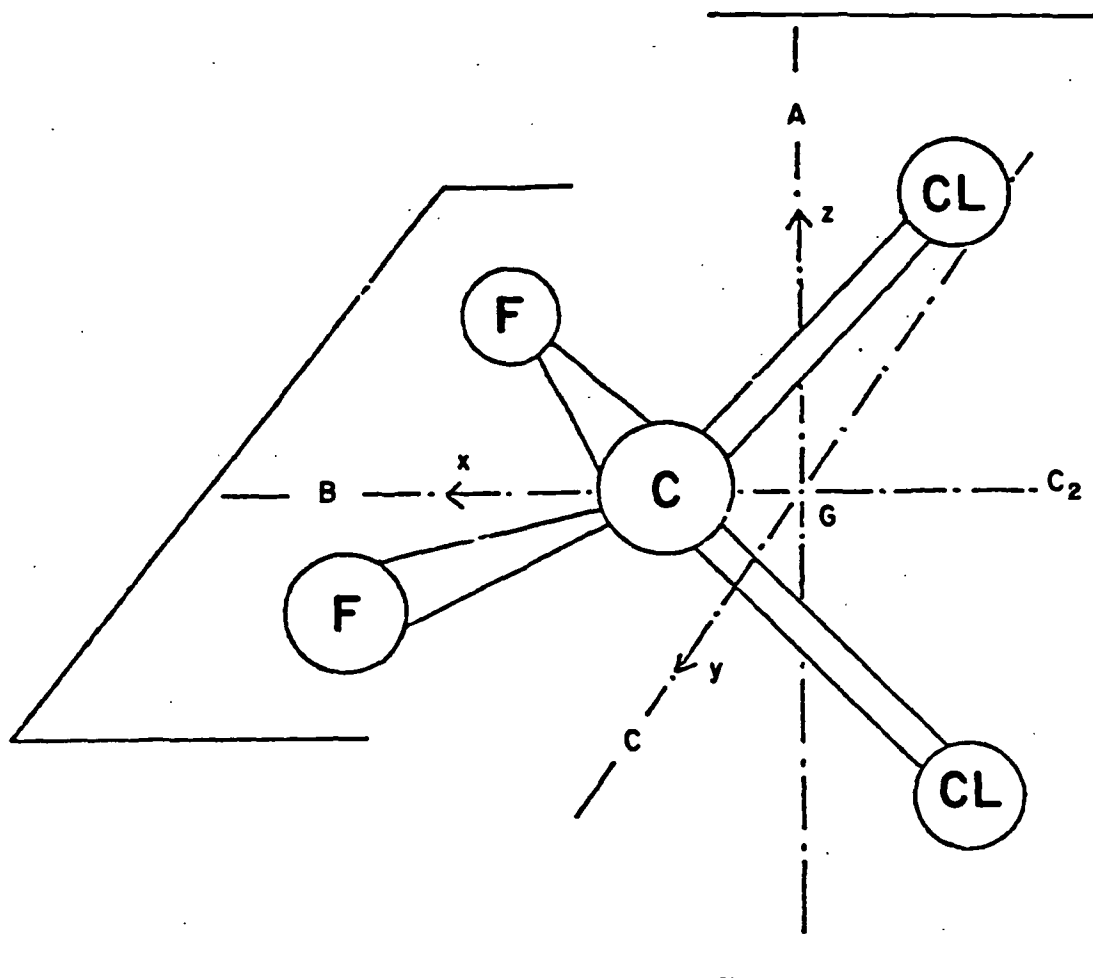


Figure 4. Geometry of CF_2 molecule. A, B, and C axes are indicated such that $I_A < I_B < I_C$.

isotopic variety. As seen in the figure, the AV-symmetry plane is the plane of the Cl-C-Cl bonds, and the BC-symmetry plane is the plane of the F-C-F bonds. The point G represents the center of mass of the molecule. If the two atoms are different isotopes, only the AB-plane remains a symmetry plane and the molecule then belongs to the C₃ point group.

Because the ν_6 band is the asymmetric stretch of the Cl-C-Cl bonds, the isotopic variations in chlorine severely complicate this spectral region near 923 cm⁻¹. Fluorine has only one isotopic form, so the ν_8 region of asymmetric F-C-F stretch is not complicated by isotopic band overlap.

Chlorine-35 and chlorine-37 exist in an abundance ratio of approximately 3:1. Thus, $\text{CF}_2^{35}\text{Cl}_2$, $\text{CF}_2^{35}\text{Cl}^{37}\text{Cl}$, and $\text{CF}_2^{37}\text{Cl}_2$ exist in a ratio of 9:6:1. In the region near 923 cm⁻¹, absorption bands of all three isotopic varieties are visible in the spectrum. The isotopic variation caused by carbon-13 also exists, but is much less a problem. No bands in the ν_6 region nor the ν_8 region have been attributed to the carbon-13 isotope in this work.

A preliminary analysis of the ν_6 band of $\text{CF}_2^{35}\text{Cl}_2$ was performed by Nordstrom et al [13]. Seven bands near 923 cm⁻¹ were located and identified. The identifications are listed in Table I.

Selected spectra collected for this effort are shown in Figure 5 and Figure 6. Table II lists the path lengths, concentrations, and optical depths used for the spectra. At the low optical depth, the

Table I. Rotation and distortion constants to order δ_K for the ground

ROTATIONAL AND DISTORTION CONSTANTS FOR $^{35}\text{Cl}-^{35}\text{Cl}$ ISOTOPE OF CF_2Cl_2			
CONSTANTS	TAKEO and MATSUMURA [§]	THIS WORK (See Text)	
A	0.1373993(13) cm^{-1}	0.1373985(5)	cm^{-1}
B	0.0880224(7)	0.0880215(5)	
C	0.0745130(7)	0.0745120(5)	
Δ_J	4.43608 E-8	1.42780 E-8	[†]
Δ_{JK}	-1.1643 E-8	-9.40335 E-9	[†]
Δ_K	5.5041 E-8	5.04247 E-8	[†]
δ_J	3.715 E-9	3.113 E-9	[†]
δ_K	0.0 (fixed)	4.5891 E-9	[†]

[§] Converted from constants given in: Harutoshi Takeo and Chi Matsumura, Bul. Chem. Soc. of Japan 50, 636 (1977).

[†] Fixed to the value suggested by Mills.

TABLE II
Sample Conditions

SAMPLE	DISTANCE (meters)	SAMPLE PRESSURE (10^{-3} torr)	PATH torr-meters
A	907	1.09	.993
B	907	.109	.0993
C	303.5	.365	.1108
D	303.5	.0916	.0278
E	303.5	.0182	.00554
F	303.5	.182	.0554
G	562.3	.0182	.01026

90 Torr of outside air added to sample G

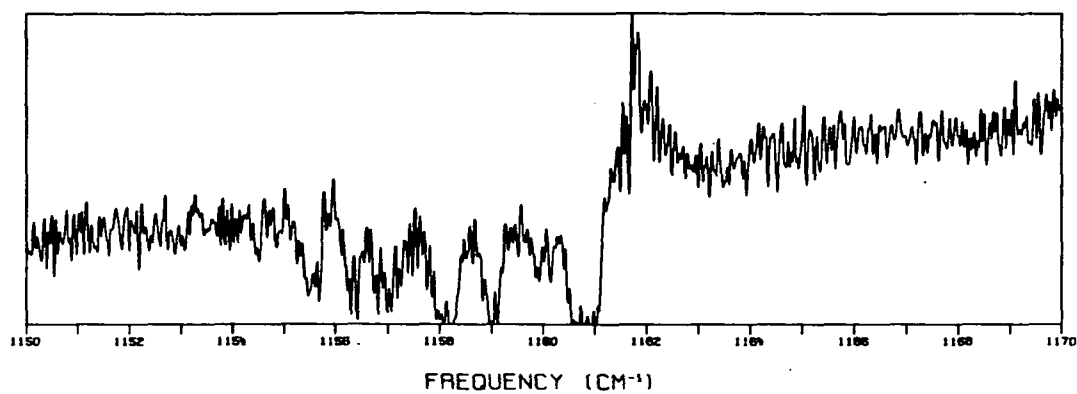


Figure 5a. SAMPLE A.

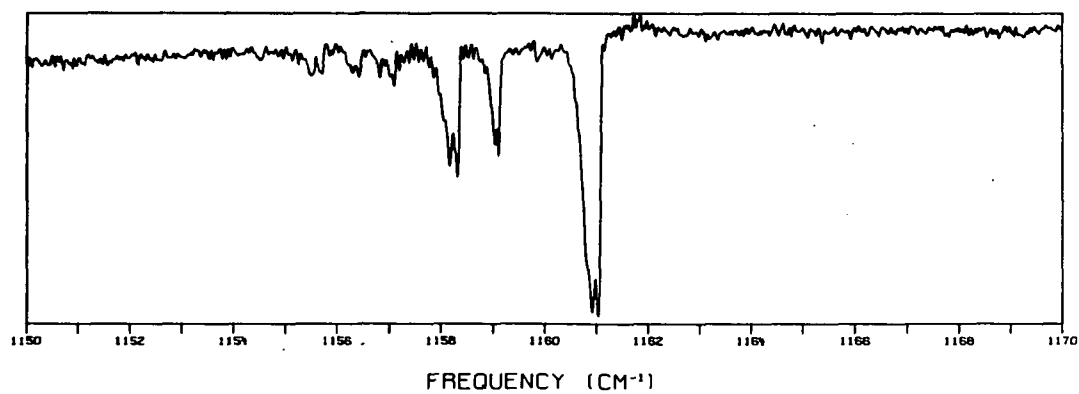


Figure 5b. SAMPLE B.

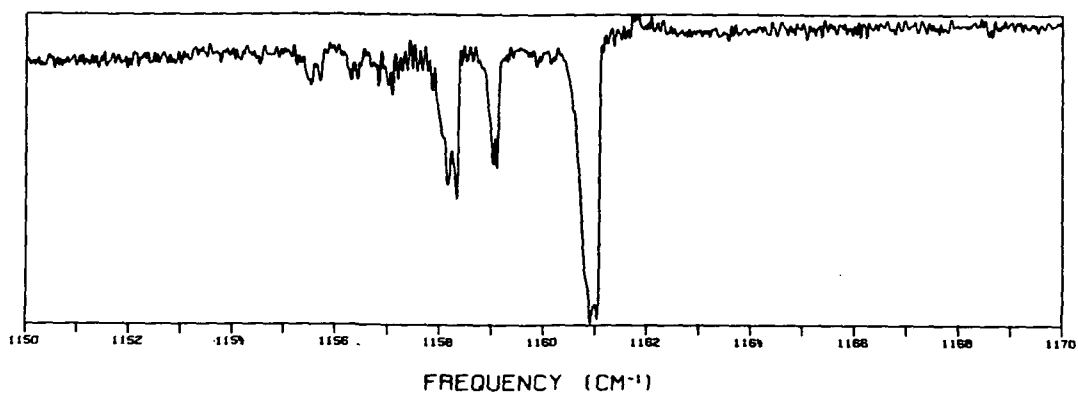


Figure 5c. SAMPLE C.

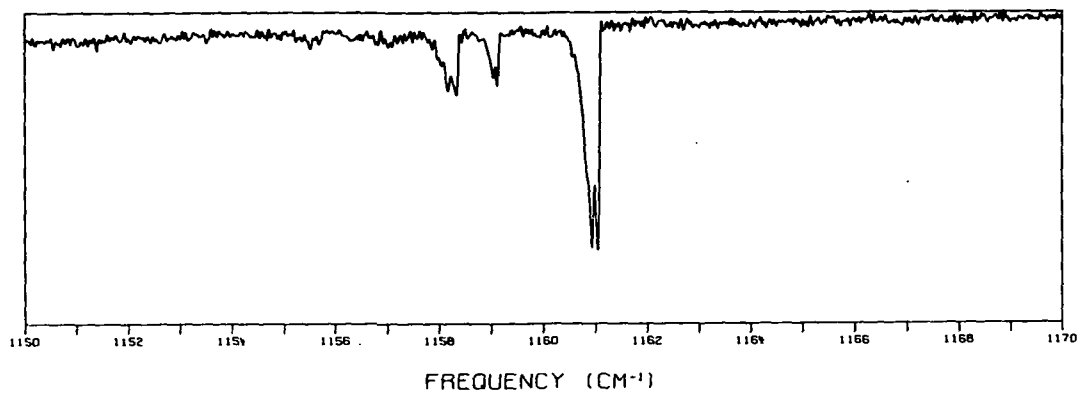


Figure 5d. SAMPLE D.

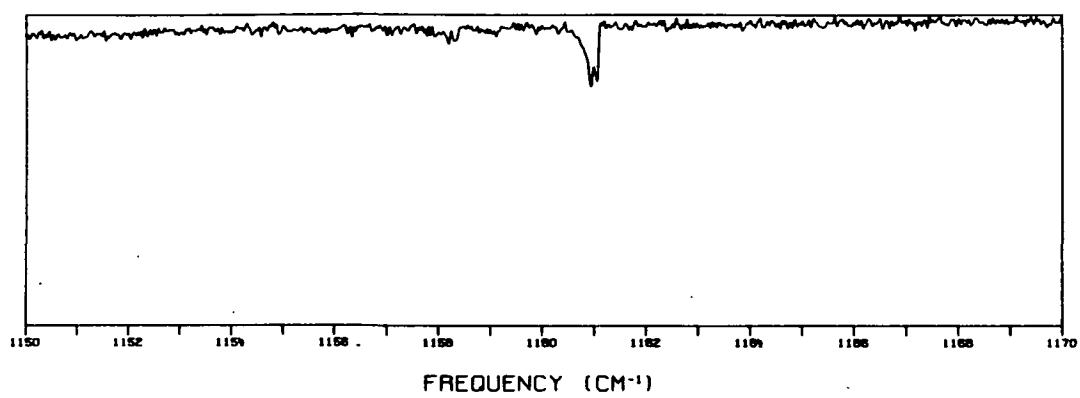


Figure 5e. SAMPLE E.

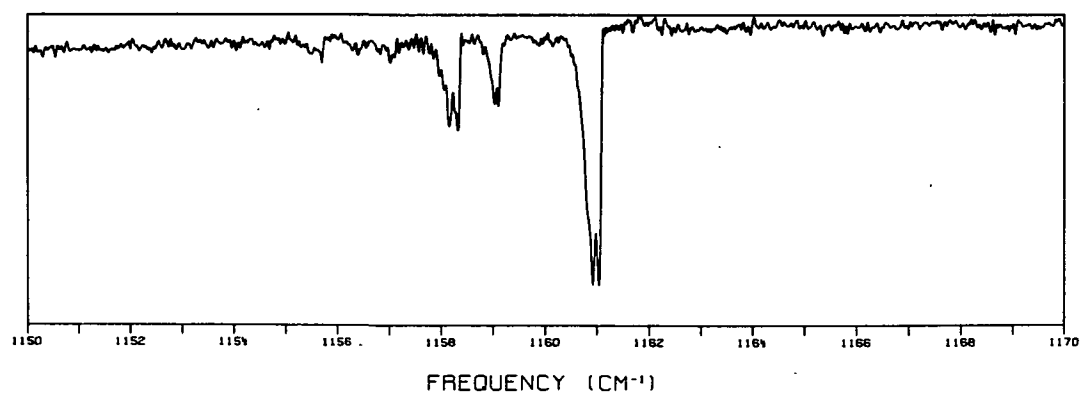


Figure 5f. SAMPLE F.

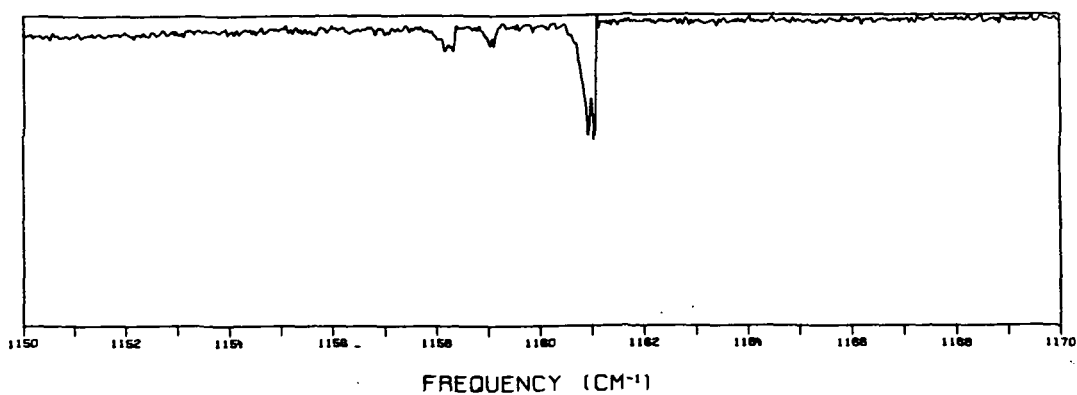


Figure 5g. SAMPLE G.

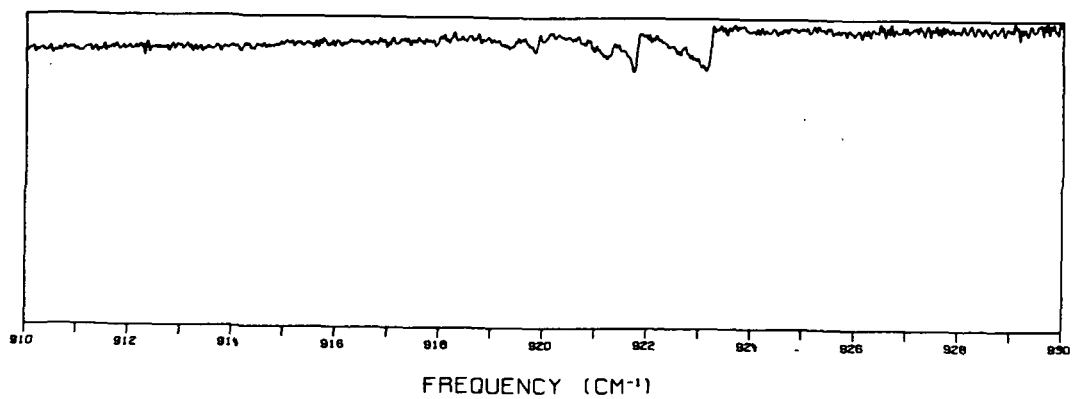


Figure 6a. SAMPLE G.

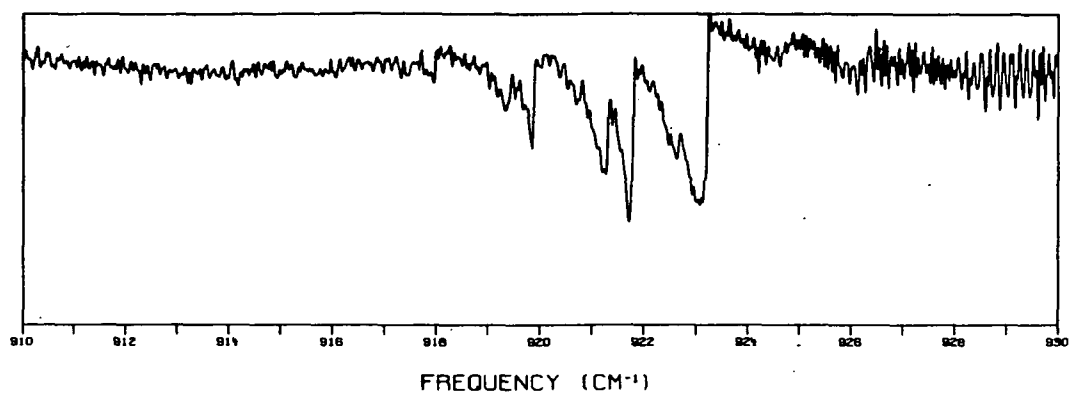


Figure 6b. SAMPLE B.

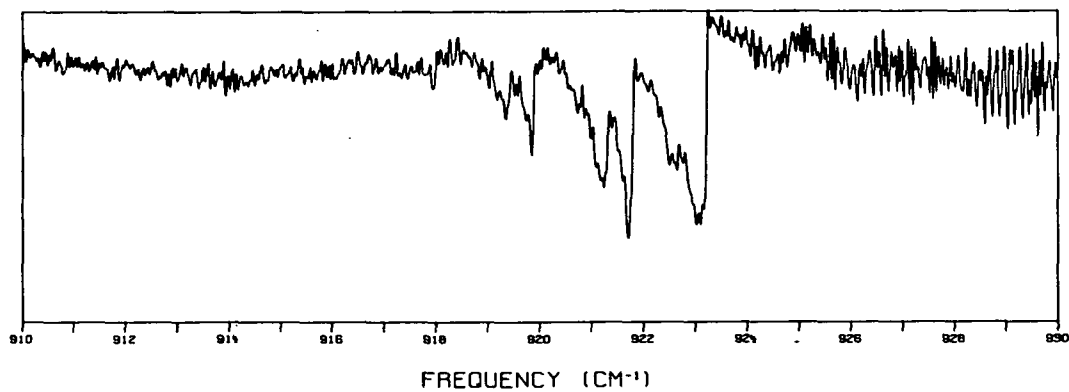


Figure 6c. SAMPLE C.

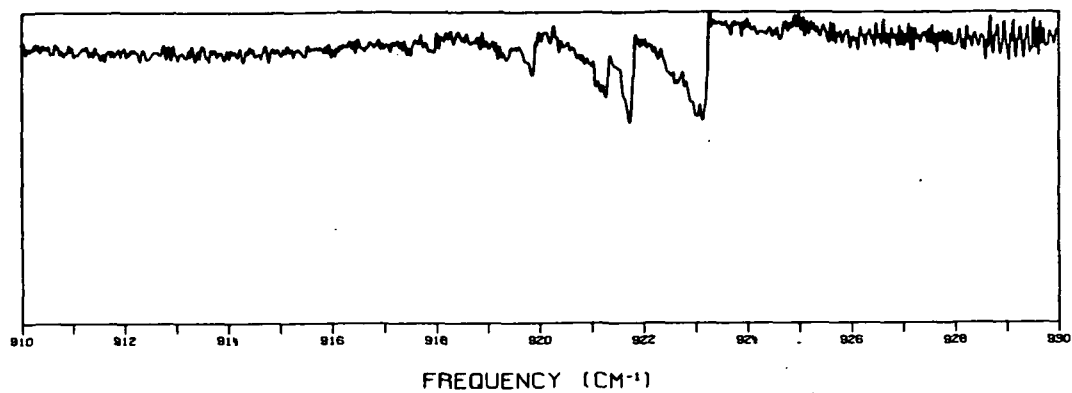


Figure 6d. SAMPLE D.

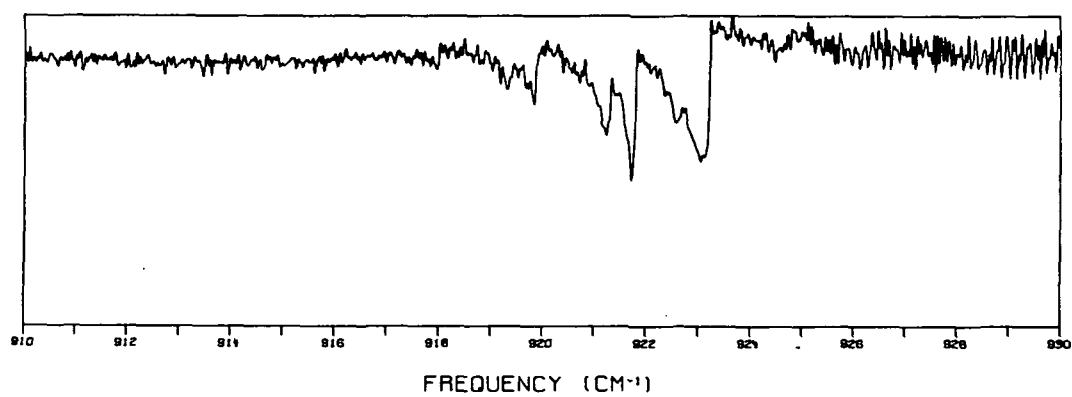


Figure 6e. SAMPLE F.

spectrum is equivalent to several parts per billion in the stratosphere seen in a long-path limb experiment such as ATMOS.

Broadening by nitrogen and air did not appreciably change the appearance of the spectra at this resolution. Under much higher resolution provided by diode lasers, however, pressure broadening affects the spectrum as shown in Figure 7.

Structure seen in the P-branch and R-branch regions of both the ν_6 and ν_8 regions is reproducible from one spectrum to another. This indicates that the structure is not noise, but actually represents rotational absorption line structure from the various overlapping bands in both regions. Furthermore, the strong Q-branch of the ν_8 band near 1161 cm^{-1} is seen to be a doublet.

Analysis of the structure for both ν_6 and ν_8 was not possible, due to the confusing overlap of absorption bands. Nevertheless, these bands are useful for optical detection of CF_2Cl_2 in the stratosphere.

IV. AMBIENT SAMPLING

In an effort to obtain samples of ambient freon and other trace gases, a cryo-condensation unit was constructed and tested, using a technique suggested by Hanst. In essence, an ambient air sample is liquified under pressure in a liquid nitrogen bath and the lower-boiling components (mainly nitrogen and oxygen) vacuum-distilled off at that temperature. The higher boiling point components, such as fluorocarbons and hydrocarbons, will be preferentially trapped in the cryogenic apparatus. Care must be taken to remove ambient water vapor and carbon

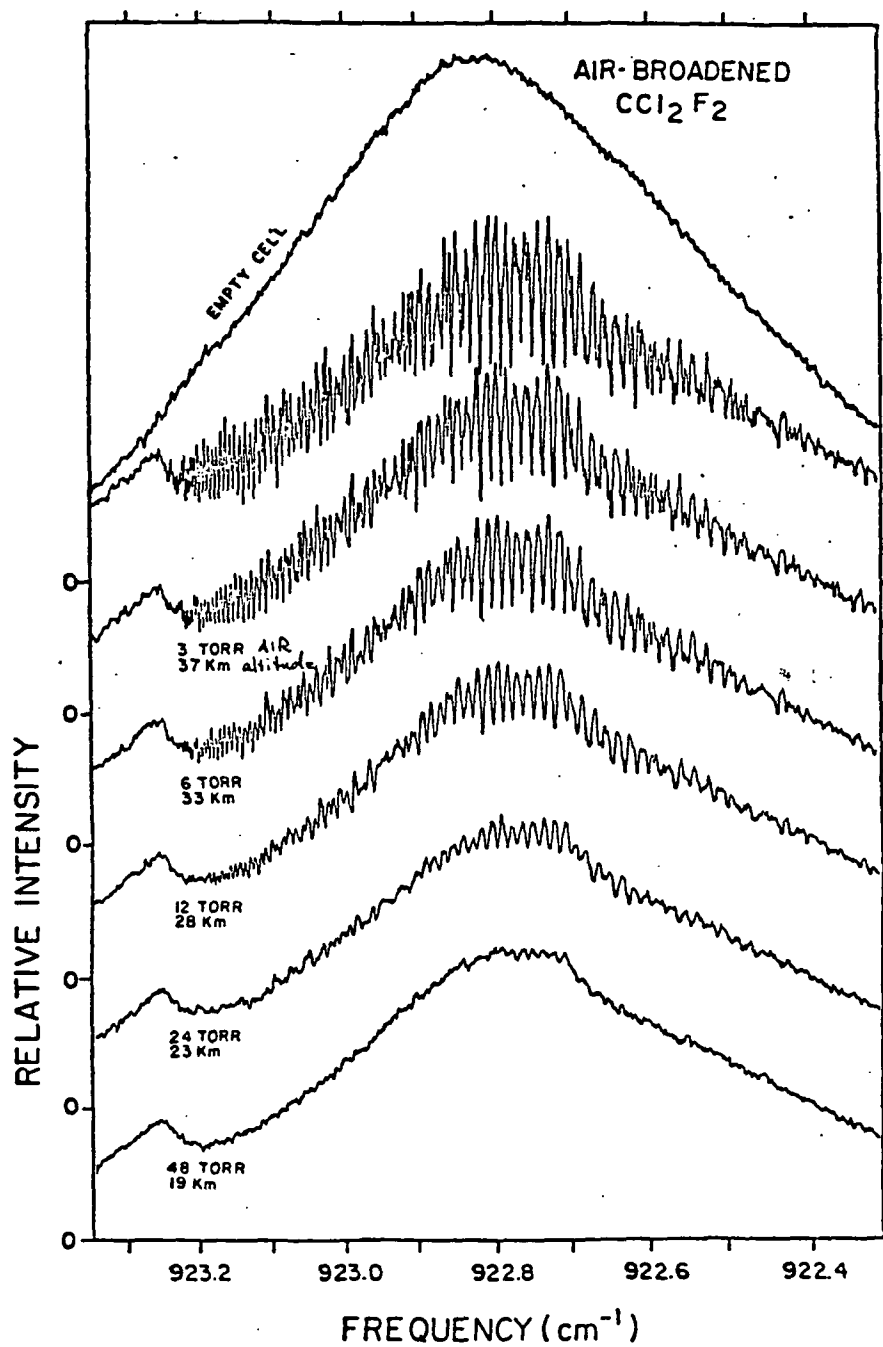


Figure 7. Effects of air broadening on a 0.2 Torr sample of CF_2Cl_2 in a 30 mm cell.

dioxide before liquifaction to avoid dangerous ice plugs, as well as to get rid of most of these high-boiling point fractions.

The cryo-condensation unit constructed included a pair of Atlas LE3N oilless compressors mounted on a 40 liter storage tank. Pumping and storage pressure were approximately 100 psi. The manifold connecting the compressors with the storage tank contained filters holding 600g of Drierite and 13g of Ascarite, for H₂O and CO₂ removal respectively. These quantities are sufficient for removal of at least four times the amount expected in a 5000 liter sample liquification.

Liquification was performed at 40 psi into a set of 9 copper tanks submerged in liquid nitrogen. A short pre-cooling coil of copper tubing substantially improved the liquification rate. Total capacity of the tanks is approximately 8 liters. They are manifolded in such a way that each set of three can be independently controlled. The usual operational method was to liquify to one set, then pump on that set while the next set was filled. Final pumping was with all three sets in parallel.

The pumping cycle should be carefully controlled, and an analysis of the effluent gases would have been helpful, but was not available. The initial 40 psi in the uncooled portion of the tubing to the tank was blown off. Presumably, most of the noncondensable components (H₂, Ne, and He) are in this portion. A vacuum pump is then connected to the three-tank manifold. Pump-off rate of the nitrogen and oxygen is strongly controlled by thermal transfer from the liquid nitrogen bath to supply the heat of vaporization. Further, the pressure must not drop

to the nitrogen triple-point of 94 torr as the resulting nitrogen solid will lose thermal contact and sublime very slowly. When the nitrogen has been substantially removed, the pressure may be reduced.

The final stages of pumping will be predominantly oxygen, with a vapor pressure of 150 torr at 77k, and the trace argon. The oxygen could be dangerous to the vacuum pump, so a vacuum regulator bled in outside air to maintain a 100 torr pressure and dilute the effluent at the vacuum pump.

When the sample tanks had been pumped to 100 torr, and would remain at that pressure when valved off, a collection tank was hooked to the system. By cooling it with liquid nitrogen and allowing the sample tanks to come to ambient temperature, the sample was cryopumped into the metal collection tank. For most test runs, this would be about 0.5 liter at STP. A second cryopumping to a pyrex flask was later performed for sample storage.

The final sample could be then introduced into the multi-pass White cell. This is not the most efficient measurement however, if the sample has reasonable vapor pressure and if pressure broadening is not a problem. For these measurements the samples were cryopumped to a 120 cm long cell 3 mm in diameter. The infrared radiation in the interferometer system is propagated through such a small diameter cell by reflection from the interior walls. Even though this is a single-pass system, the pressure-path length product can be substantially improved for a very small sample, if sample pressure is not a concern. For the particular combination concerned here, the White

cell had a diameter 200 times greater than the internal reflection cell, or a cross sectional area 4×10^4 greater. The multi-passing factor of 100 for the White cell still makes it 400 times less sensitive in total absorption. This ratio is insensitive to White cell length except insofar as it affects the initial optical design and subsequent chamber diameter.

The resulting spectra showed traces of Freon 12, C_2H_2 , N_2O , and CH_4 . The freon concentration was estimated at 120 ppt of the original sample. None of the alcohols were observed in the final sample.

REFERENCES

- [1] M. J. Molina and F. S. Rowland, *Nature* 249, 810 (1974).
- [2] N. E. Hester, E. R. Stephens, and O. C. Taylor, *J. Air Pollution Control Assoc.* 24, 591 (1974).
- [3] N. E. Hester, E. R. Stephens, and O. C. Taylor, *Environ. Sci. Technol.* 9, 875 (1975).
- [4] L. E. Heidt, R. Lueb, W. Pollock, and D. H. Ehholt, *Geophys. Res. Letters* 2, 445 (1975).
- [5] W. J. Williams, J. J. Kasters, A. Goldman, and D. G. Murcray, *Geophys. Res. Letters* 3, 379 (1976).
- [6] R. J. Nordstrom, J. H. Shaw, W. R. Skinner, W. H. Chan, J. G. Calvert, and W. M. Uselman, *Appl. Spectros* 31, 224 (1977).
- [7] C. M. Bradford, F. H. Murcray, J. W. Van Allen, J. N. Brooks, D. G. Murcray, and A. Goldman, *Geophys. Res. Letters* 3, 387 (1976).
- [8] R. A. McClatchey, W. S. Benedict, S. A. Clough, D. E. Burch, R. F. Calfee, K. Fox, L. S. Rothman, and J. S. Garing, *AFCRL Atmospheric Absorption Line Parameters Compilation*, Report No. AFCRL-TR-73-0096, *Environmental Research Papers*, No. 434, (1973).
- [9] F. S. Mills, "Absorption of Deuterium Fluoride Laser Radiation by the Atmosphere," No. 4054-3, Rome Air Development Technical Report, Atmospheric Sciences Laboratory, ECOM-74-4, December, 1974.
- [10] S. A. Clough, F. X. Kneizys, and J. H. Chetwood, Jr., "Algorithm for the Calculation of Absorption Coefficient -Pressure Broadened Molecular Transitions," AFGL-TR-77-0164, July 1977.
- [11] J. C. Fontanella, A. Girard, L. Biramont, and N. Louishard, *Appl. Opt.* 14, 825 (1975).
- [12] S. Giorgianni, A. Gambi, L. Franco, and S. Ghersetti, to be published in *J. Molec. Spectros.*
- [13] NSF Exchange of Scientists Program, Division of International Programs, 1800 G St. N.W., Washington, D.C. 20550.

- [14] H. Takeo and C. Matsumura, Bull. Chem Soc. Japan 50, 636 (1977).
- [15] C. Fu Su and E. L. Beeson, Jr., J. Chem. Phys. 66, 330 (1977).
- [16] I. M. Mills, private communication.
- [17] E. K. Plyler and W. S. Benedict, J. Res. Nat. Bureau Stands, 47, 202 (1951).
- [18] A. Goldman, F. S. Bonomo, and D. G. Murcray, Geophys. Res. Letters 3, 309 (1976).
- [19] D. E. Jennings, Geophys. Res. Letters 5, 841 (1978).
- [20] A review of SISAM is provided in "Montage et Mise au Point d'un Spectrometre SISAM. Son Utilisation a l'Etude du Spectra d'ABsorption du Chlorure de Methyle" by M. Morillon-Chapey.
- [21] D. E. Jennings, J. H. Hillman, and W. H. Weber, Optics Letters 2, 157 (1978).